

OIL PRODUCTION BY HIGH-PRESSURE THERMAL TREATMENT OF BLACK LIQUORS: AQUEOUS-PHASE PRODUCTS

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ABSTRACT

Liquid-phase treatment of black liquors, from alkaline pulping, at 300 - 350 °C in a reducing atmosphere results in the formation of an oil-like product, which separates out from an aqueous phase containing the inorganic constituents. The process has several potential forms of application. This study was conducted in support of the development of one such application: a new recovery system for the kraft pulping process. Thermal treatment experiments were performed using different reactant gases. On the basis of analyses of the resultant gaseous and aqueous phases, the main reactions leading to aqueous-phase products were elucidated. This information was used to advantage in the compilation of a process scheme for the recovery of the cooking chemicals from the aqueous phase.

INTRODUCTION

A process producing liquid fuels from the organic matter of the black liquors from alkaline pulping is being developed at the Laboratory of Fuel Processing and Lubrication Technology, Technical Research Centre of Finland (VTT). The central operation in the process is the liquid-phase thermal treatment of black liquor at 300 - 350 °C under a reducing atmosphere (1). The treatment results in the formation of a hydrophobic oil which separates out from an aqueous phase containing the inorganic constituents (Figure 1).

The process can be applied in either of two basic ways:

- as a method to produce oil in conjunction with the kraft pulping process,
- as an entirely new system for recovering the cooking chemicals and energy from kraft spent liquors.

The first type of application exploits the favourable properties of black liquor as a feedstock for high-pressure conversion. In comparison to solid biomass, the advantages of black liquor as a feedstock include:

- no pretreatment required. Black liquor can be directly pumped into the reactor at dry solids concentrations as high as 60 %,
- black liquor contains alkaline compounds known to catalyze conversion reactions,
- cellulose, the most valuable component of wood, is not subjected to the conversion process.

In this type of application, the kraft cooking chemicals are recovered using the traditional method which is centred around the Tomlinson recovery boiler. Additional plant fuel (wood waste, peat, coal) is needed. Preliminary economic evaluations have indicated that this type of oil production process would be economic if oil prices were at their 1985 level.

In the second type of application, the Tomlinson recovery boiler is replaced by a safer and thermally more efficient recovery system, in which the oil produced by thermal treatment is used as plant fuel. This type of process is, in many respects, similar to the Hydrolysis Recovery Process developed by the St.

Regis Paper Company, USA (2), the essential difference being the use of a reducing atmosphere in the VTT process. The experiments described here-in were undertaken in support of the development of this second type of process.

The specific objectives of the present study were to elucidate the main reactions leading to aqueous-phase products, and, by applying this knowledge, to establish process schemes for the recovery of the cooking chemicals from the aqueous phase. Because the composition of the aqueous phase is dependent upon the composition of the reactant gas, several different gases were employed in these experiments.

It should be mentioned that research on conversion of black liquors is but a part of a wider biomass conversion program being undertaken at our laboratory. Other major parts to this program are:

- development of fixed-bed and fluid-bed gasification processes, including combined cycle power generation applications,
- supportive research for the first synthesis-gas plant using peat or wood as feedstock (the peat-ammonia plant of the Finnish company, Kemira),
- basic research on direct liquefaction processes for peat and wood (high-pressure liquefaction and flash pyrolysis),
- development of low-waste technologies.

EXPERIMENTAL

The kraft black liquor, employed in the experiments, originated from a laboratory cook of Scots pine (*Pinus sylvestris*). An analysis of the liquor is given in Table 1.

Table 1. Analysis of kraft black liquor¹.

	% of dry solids
Organic matter	78.9
Total Na	18.4
NaOH	3.0
Na ₂ S	5.5
Na ₂ SO ₄	0.04
Na ₂ CO ₃	1.1

¹ dry solids content of 30 %

A later batch of liquor, prepared in a similar way, was also analyzed for volatile acids (formic and acetic acids) and lactic acid, which are present as sodium salts in the liquor. On the basis of the analyses it can be concluded that the contents of these acids in the feed liquor used in the present experiments were approximately 6 % om, 4 % om, and 4 % om respectively, where % om denotes the percentage of black liquor organics.

The experiments were conducted in a 1-litre autoclave. In a typical experiment 500 ml of black liquor was placed in the autoclave and reactant gas was charged at sufficient pressure (5 - 9 MPa) to result in a total pressure of about 20 MPa at the reaction temperature. The autoclave was then heated at a rate of about 5 °C/min. A fixed time-at-temperature of 45 min was chosen for these experiments.

At the end of the reaction period, the autoclave was rapidly cooled, after which gases were released, measured, and analyzed. The organic phase and the aqueous

phase were separately recovered from the autoclave and weighed. The pH of the aqueous phase was measured. In many of the experiments the aqueous phase was also analyzed for formic, acetic, and lactic acids (present as sodium salts) and for CO_2 (chemically bound in sodium carbonate or bicarbonate). The former were analyzed by gas chromatography as their benzyl esters (3), the latter by measuring the amount of CO_2 liberated upon acidification with excess mineral acid.

The primary experiments were those employing either carbon monoxide or hydrogen as reducing gas. Two temperatures, 300 °C and 350 °C, were investigated. Experiments employing non-reducing carbon dioxide were also conducted in order to assess whether alkali neutralization by the reactant gas plays an important role in the thermal treatment process. One experiment was performed with a reactant gas of composition similar to that of a typical low-calorific fuel gas (producer gas) generated by gasification of biomass with air.

RESULTS AND DISCUSSION

The main experimental results are presented in Table 2.

Table 2. Results of autoclave experiments. Time-at-temperature: 45 min.

Experiment	1	2	3	4	5	6	7	8
Reactant gas	CO	CO	H_2	H_2	H_2	CO_2	CO_2/H_2 ¹	Producer gas ²
Temperature, °C	300	350	300	350	350	350	345	350
Pressure, MPa	20	26	18	22	22	24	26	26
Yields, % of black liquor organics (% om)								
oil ³	24.9	26.9	0	23.2	22.6	0	22.1	20.2
bitumen ⁴	35.1	25.6	80.7	36.5	33.4	81.4	34.1	36.5
CO ⁵	30.1	32.1	0.4	2.4	2.4	0.6	5.2	3.9
H_2	0.5	0.7	- 0.5	- 0.3	- 0.2	0	- 0.3	- 0.1
CO	- 31.8	- 28.6	0	0	0	0	0	- 3.8
CH_x -gases	0.4	0.6	0.1	0.7	0.8	0.7	1.0	0.7
H_2S	1.4	1.1	0.3	0.5	0.4	1.0	ND	0.4
CO_2 /aqueous ⁶	2.0	19.0	10.0	ND	18.0	ND	19.0	ND
formic acid ⁷	35.7	10.6	6.2	ND	4.6	1.6	ND	ND
acetic acid ⁷	4.5	3.9	4.1	ND	3.8	3.9	ND	ND
lactic acid ⁷	1.3	0.3	1.5	ND	0.3	0	ND	ND
Aqueous-phase pH	8.5	8.5	10.2	9.5	9.4	8.9	8.4	9.1

¹ 60 % CO_2 , 40 % H_2

² 14 % CO_2 , 51 % N_2 , 17 % H_2 , 18 % CO

³ organic product as oil layer

⁴ heavier organic product

⁵ in gaseous phase

⁶ in aqueous phase as HCO_3^- or CO_3^{2-}

⁷ present as sodium salts

ND: not determined

Formation of oil phase

In this experimental program, complete separation of the organic product as a single oil layer was not achieved, even when reaction conditions were apparently similar to those successfully employed in other types of reactor in earlier development work ($\text{CO}/300^\circ\text{C}$) (1). In experiments in which an oil layer was

formed, part of the organic matter was also converted into a bitumen-like material. It was assumed that this separation of the organic product into two phases was dependent on certain physical parameters of the reaction system. This assumption has since been confirmed. In this study, concerned with reactions of aqueous-phase constituents, efforts were not expended in optimizing physical conditions for oil-layer formation. In Table 2, the yields of "oil" and "bitumen" are reported separately.

The oil yield data of Table 2 indicate that, at 300 °C, CO was effective in producing a distinctly oil-like product but H₂ was not. At 350 °C, H₂ was also an effective reactant gas, as were mixtures of CO and H₂ with other gases (for example, "producer gas"). CO₂, on the other hand, was not effective, confirming that the most important function of the reactant gas is to reduce organic matter in the liquor.

Interactions between gaseous and aqueous components

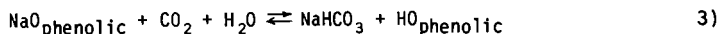
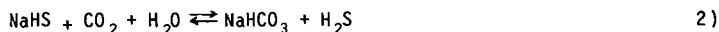
In all experiments the thermal treatment led to a decrease in the black liquor alkalinity, the final pHs being in the range 8 - 10 (Table 2). The chief neutralizing agents were the gases CO and CO₂. The decrease in alkalinity was least extensive in experiments employing hydrogen as reactant gas, but it was nonetheless quite significant, particularly at 350 °C (Expts. 4 and 5). In these cases, the neutralizing agent was CO₂, a product of the thermal decomposition of the organic matter (decarboxylation).

The electrolyte systems of kraft black liquor are well known (4). In principle this data can be applied to the product mixture of the thermal treatment process, allowing the following conclusions to be drawn:

1. In all cases, sulphur is present as HS⁻ in the aqueous phase, the final pHs (8 - 10) being lower than the pK_a for HS⁻ (~ 13.5) and higher than the pK_a for H₂S (~ 7). Very little H₂S should be formed.
2. HCO₃⁻ predominates over CO₃⁼, particularly at the lower end of the observed pH range. pK_a for HCO₃⁻ is ~ 10.
3. The phenolic hydroxyl groups of the lignin molecules are largely in an unionized condition, i.e. not bound to the sodium ion (pK_s: 9.5 - 11).
4. The carboxyl groups, which do not decompose during the thermal treatment, remain ionized (pK_s: 3 - 5). The three main fractions of the organic matter of the black liquor are lignin, aliphatic acids, and extractives. The aliphatic acid fraction contains the bulk of the carboxyl groups, but some are also encountered in the other fractions (5).

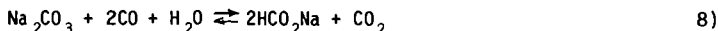
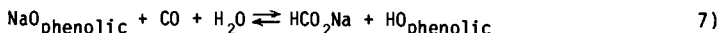
However, it should be noted that, because of mass transfer limitations, equilibrium between the gas and liquid phases is not necessarily established during all phases of the treatment process. For example, considerable amounts of H₂S were evolved during the treatment, the lower the pH the more H₂S (Table 2), indicating a higher pK_a value at the reaction temperature, and, after the rapid cool-down, lack of equilibrium between H₂S in the gas phase and H₂S in the aqueous phase.

When the neutralizing agent is CO₂, the main neutralization reactions can be written as follows:





When CO is the neutralizing agent, the equations become:



The results in Table 2 indicate that, at 350 °C, Reactions 1 to 4 occurred to a significant extent in all atmospheres. In the CO atmosphere, a significant amount of formate was also produced (Reactions 5 to 9). At 300 °C, the aqueous-phase composition in the CO experiment was considerably different from that in the H₂ experiment. In the CO atmosphere, a very large quantity of formate was formed. The increase compared to the CO/350 °C experiment was presumably due to a shift in the equilibria of Reactions 8 and 9. In the H₂ atmosphere at 300 °C, carbonate formation, although still significant, was less than at 350 °C (less decarboxylation of organic matter).

Stability of organic acid salts

A large fraction of the organic material of black liquor is comprised of aliphatic acids (5). In addition to the acids analyzed, there are significant quantities of less volatile aliphatic hydroxy acids. The acids, present as sodium salts in black liquor, are formed from wood polysaccharides during pulping. At the present time, the fate of the hydroxy acid components, other than lactic acid, during the thermal treatment process is not known with certainty. A recent study of cellulose conversion in alkaline solution suggests, however, that these components will not be converted into water-insoluble product, that is, oil, under these conditions (6). This is consistent with the energy yields of organic phase (oil and bitumen) observed in the present experiments. The yields are what one would expect if the organic phase were to originate almost entirely from the lignin fraction of black liquor. Forthcoming experiments will aim at confirming the origins of the oil product.

The present results (Table 2) indicate that sodium acetate was rather stable under the conditions of the thermal treatment, while sodium lactate decomposed to a large extent. Sodium formate decomposed in the CO₂ atmosphere, presumably due to a shift to the left of the equilibria of Reactions 8 and 9. In the H₂ atmosphere, formate was fairly stable. In this case, the decomposition of formate to carbonate was probably prevented by the following reaction (7):

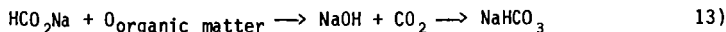


Consumption of reducing gas

From the point of view of oil formation, the most important reactions of CO or H₂ are the reduction reactions:



Sodium formate can also function as a reductant in a similar way (8):



However, the results of the $\text{H}_2/300^\circ\text{C}$ experiment suggest that the formate present in the black liquor feedstock (at 6 % om concentration) is not an effective reductant.

In addition to its being consumed as a reductant, CO is consumed in partial neutralization of black liquor alkalinity (Equations 5 to 9) and in production of H_2 by the water-gas-shift reaction:



From the data of Table 2, it has been possible to establish the consumption patterns of CO at 300°C and 350°C (Table 3).

Table 3. Consumption of CO.

		% of black liquor organics (% om)	
		CO/300 $^\circ\text{C}$	CO/350 $^\circ\text{C}$
I	Neutralization	18	3
II	Reduction	7	16
III	Shift	7	10
	Total	32	29

The total level of CO consumption, about 30 % om, is equivalent to a H_2 consumption of 2.1 % om, which is a much higher value than that observed in H_2 experiments: 0.3 - 0.5 % om (Table 2).

IMPLICATIONS FOR PROCESS DEVELOPMENT

The aqueous phase leaving the thermal treatment reactor contains the following compounds:

- NaHS ($\rightleftharpoons \text{Na}_2\text{S}$)
- NaHCO_3 ($\rightleftharpoons \text{Na}_2\text{CO}_3$)
- Sodium salts of aliphatic acids, with formate and acetate as two main components. The formate content is considerable when the reactant gas is CO .
- Other organic compounds in smaller amounts.

The organic acid salts and other organic compounds cannot be recycled, in their entirety, to the cooking stage. If not purged from the system, they will quickly build-up in concentration in the cooking liquor and retard the delignification reactions. Furthermore, particularly if the formate concentration is high, there may be insufficient sodium for binding to the hydroxide ion. In fact, various possibilities of converting sodium formate directly into sodium hydroxide were investigated in this study, but none of these proved to be technically feasible.

One example of a workable scheme for the recovery of chemicals is depicted in Figure 2. A part of the aqueous phase leaving the thermal treatment stage is recycled through a wet oxidation reactor where organic matter is oxidized to carbonate, CO_2 , and H_2O . The heat produced is employed in heating the feed

stream to the thermal treater. The rest of the aqueous phase is recausticized in the conventional way. In addition to the normal components of kraft green liquor, this liquor contains NaHCO_3 and some organic matter. The presence of organic matter should be an advantage because, according to the literature, a small but significant increase in pulp yield can be expected (2). The presence of NaHCO_3 will lead to a higher lime requirement in the recausticizing stage.

Wet oxidation is quite an economic process step in this scheme because the feed stream to it is already at the required temperature and pressure. Sulphide will be oxidized to sulphate, but it should be reduced again to sulphide in the subsequent heat treatment stage. This latter reaction will be investigated experimentally in the near future. For reasons of low gas consumption and low gas cost, producer gas is the reducing gas proposed for the scheme of Figure 2.

Preliminary economic evaluations of this scheme have indicated that it would be more economic than the conventional recovery process, particularly if a higher pulp yield were obtained. This process would also have a higher thermal efficiency than the conventional process.

CONCLUDING REMARKS

The black liquor treatment process being developed at VTT has several promising forms of application. The work described in this paper has furthered the development of one such application: a new recovery system for the kraft pulping process. Current research is being directed at gaining a better understanding of the oil-forming reactions occurring during thermal treatment.

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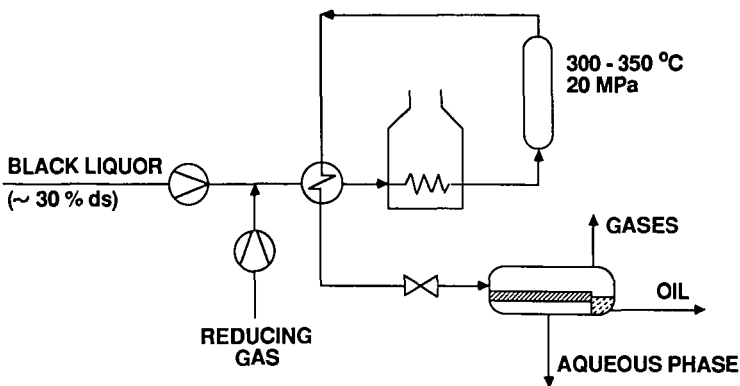


Figure 1. The thermal treatment process for black liquors.

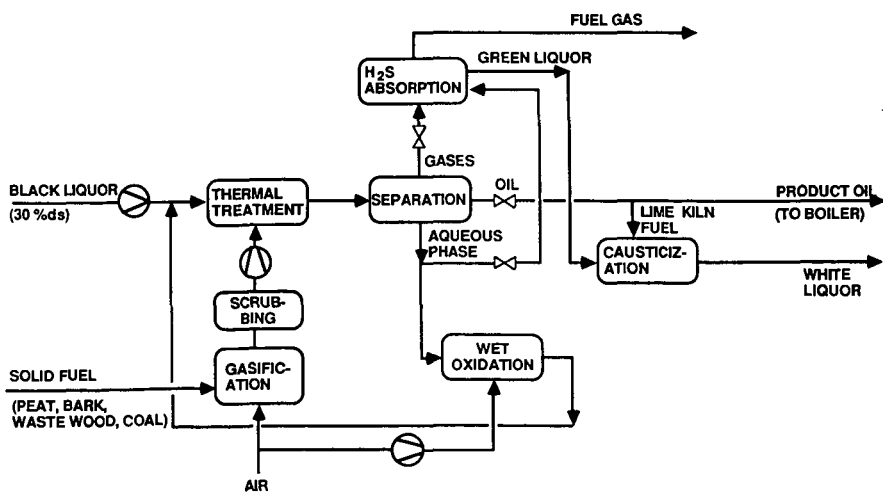


Figure 2. Preliminary scheme for a new kraft recovery process.